## **Caption list**

Figure 1.

Dehydrogenation of n-paraffins : GC×GC chromatograms of the feed (A) and the products at 10% (B) or 20% (C) conversion. Experimental conditions : see Table 1. The repetitive pattern representing the distribution of isoparaffins (I), olefins (O), diolefins (diO), and aromatics (A) in the elution zone of a normal paraffin (nP), with the same carbon atoms (n), is enhanced in the insert in Fig. 1-C. Identification : 1 ; n-nonane ; 2. n-decane ; 3. n-undecane ; 4. n-dodecane ; 5. n-tridecane ; 6. n-tetradecane ; 7 n-pentadecane ; 8. ethybenzene ; 9. nonene-1 ; 10. n-propylbenzene ; 11. 1-methyl-3-n-propylbenzene ; 12. n-butylbenzene ; 13. 1-methyl-2-n-propylbenzene ; 14. n-pentylbenzene ; 15. n-hexylbenzene ; 16. n-heptylbenzene ; 17. naphthalene ; 18. 2-methylnaphthalene ; 19. 1-methylnaphthalene.

## Figure 2.

Dehydrogenation of n-paraffins : chromatograms of the product converted at 20% obtained in 1D-GC (A) and in GC×GC (B). The elution zone of naphthalene is circled with a dotted line and has been highlighted in the insert of Figure 2-B. Naphthalene is indicated with the symbol \*. Experimental conditions : see Table 1 (2-B) and Table 2 (2-A).

## Figure 3.

GC×GC analysis of a Fischer Tropsch product. Experimental conditions : Table 1. The repetitive pattern representing the distribution of isoparaffins, olefins, and alcohols in the elution zone of a normal paraffin is enhanced in the upper left part of the chromatogram.

Figure 4.

GC×GC chromatogram of a product of oligomerization. Experimental conditions : see Table 1. The elution zone of alkylbenzenes is framed with a dotted line.







Figure 1



Figure 2









**Table I**. Experimental conditions used in GC×GC.

Conditions applied for each analysis			
First dimension column	PONA (20m×0.2mm; 0.5µm)		
Injection			
Temperature	280°C		
Split	1:200		
Injected volume	0.5µl		
Detection			
Temperature	300°C		
Gases	Air : 400 ml/min ; Hydrogen : 35 ml/min ; Helium : 25 ml/min		
Acquisition rate	100 Hz		
Modulation period	4 s		
	Additional conditions		
<b>PIONA</b> tost mixture	Additional conditions		
Second dimension column	<b>RPX50</b> (0.1mm i $d \div 0.1$ um)		
Second dimension column	or BPX70 (0.1mm i.d., 0.1 $\mu$ m)		
	or CPWay (0.1mm i.d. $(0.1 \mu m)$		
Length $2^{nd}$ column (cm)	110		
Pressure $(kP_2)$	2.5		
Temperature	$T = 50^{\circ}C \pm 2^{\circ}C / \min = 150^{\circ}C$		
remperature	$T=50^{\circ}C+2^{\circ}C/min \rightarrow 150^{\circ}C$		
	$011-30C+3C/11111\rightarrow 150C$		
Dehydrogenation of n-para	ffins		
Second dimension column	BPX50 (1 1m×0 1mm i d : 0 1µm)		
Temperature	$T=50^{\circ}C+2^{\circ}C/min\rightarrow 170^{\circ}C$		
Pressure (kPa)	2.5		
Tressure (III u)	_10		
Fischer Tropsch			
Second dimension column	BPX50 (1.1m×0.1mm i.d.; 0.1µm)		
Temperature	$T=50^{\circ}C+2^{\circ}C/min\rightarrow 280^{\circ}C$		
Pressure (kPa)	2.5		
Oligomerization			
Second dimension column	CPWax (1.1m×0.1mm i.d.; 0.1µm)		
Temperature	$T=50^{\circ}C+2^{\circ}C/min\rightarrow 250^{\circ}C$		
Pressure (kPa)	2.5		

**Table II**. Conditions used in 1D-GC for the PIONA test mixture (a) and petrochemicals analyses :Dehydrogenation of n-paraffins (b), Fischer Tropsch (c) and Oligomerization (d).

Column		PONA (50m×0.2mm; 0.5µm)
Oven temperature	9	$40^{\circ}\text{C}+2^{\circ}\text{C/min} \rightarrow 280^{\circ}\text{C} + 60\text{min}^{\text{a,b}}$ $35^{\circ}\text{C}+10\text{min}+1.1^{\circ}\text{C/min} \rightarrow 114^{\circ}\text{C} + 1.7^{\circ}\text{C/min} \rightarrow 300^{\circ}\text{C}^{\text{c,d}}$
Pressure		2 kPa
Injection	Temperature	280°C <sup>a, b, d</sup> 300°C <sup>c</sup>
	Split flow	200 ml/min
	Injected volume	0.5µl
Detection	Temperature	300°C <sup>a, b, d</sup> 350°C <sup>c</sup>
	Acquisition rate	5Hz